5 Growing season fluxes from a high latitude wetland

Although high-latitude wetlands are not anticipated to be a major source or sink of CH_3Br or CH_3Cl, it is important that CH_3Br and CH_3Cl fluxes from these areas are quantified in order to constrain CH_3Br and CH_3Cl budgets and to make predictions about future flux patterns in a changed climate. Prior to starting this thesis, CH_3X had never before been investigated from high latitude ecosystems. Since the beginning of this thesis two studies have published their findings of CH_3X fluxes from tundra ecosystems (*Rhew, et al.*, 2007; *Teh, et al.*, 2009), a distinct ecosystem from wetlands. These studies did not, however, include measurements over the full growing season.

Seasonal and diurnal trends in CH_3Br and CH_3Cl fluxes from non-polar ecosystems have been reported in a number of studies (*e.g. Redeker et al.*, 2000; *Rhew et al.*, 2002; *White et al.*, 2005; *Drewer et al.*, 2006; *Manley et al.*, 2006), but there has been no consistent evidence for external parameters driving CH_3Br or CH_3Cl fluxes across all ecosystem types; individual studies have suggested that light (*Drewer et al.*, 2006), temperature (*Rhew et al.*, 2000; *Rhew et al.*, 2002; *Redeker and Cicerone*, 2004), or soil pore-water saturation (*Redeker and Cicerone*, 2004) may affect emissions. In Arctic Alaskan tundra it was found that drained sites had greater rates of CH_3Br and CH_3Cl uptake than flooded sites in both coastal and inland areas (*Rhew et al.*, 2007; *Teh et al.*, 2009), with water table depth correlating most strongly with CH_3Cl and CH_3Br net uptake (*Teh et al.*, 2009).

In this study, CH_3Br and CH_3Cl fluxes were measured at a number of sites in sub-Arctic wetland near Abisko, in northern Sweden throughout the 2008 growing season (June–September), including a number of intra-daily flux measurements. Data for external parameters including air temperature, ground temperature, enclosure temperature and photosynthetically active radiation (PAR) were also collected.

5.1 Sampling sites

Flux measurements were undertaken in five sub-Arctic wetland areas in the vicinity of the Abisko Scientific Research Station (ANS), Abisko, Sweden (68˚28′N 18˚49′E).

The general sampling area and the individual sampling sites are shown in Figure 5.1. An initial study was carried out in August 2007 (for CH_3Br only) and a longer, seasonal study was carried out from June to September 2008 to capture the short sub-Arctic growing season.

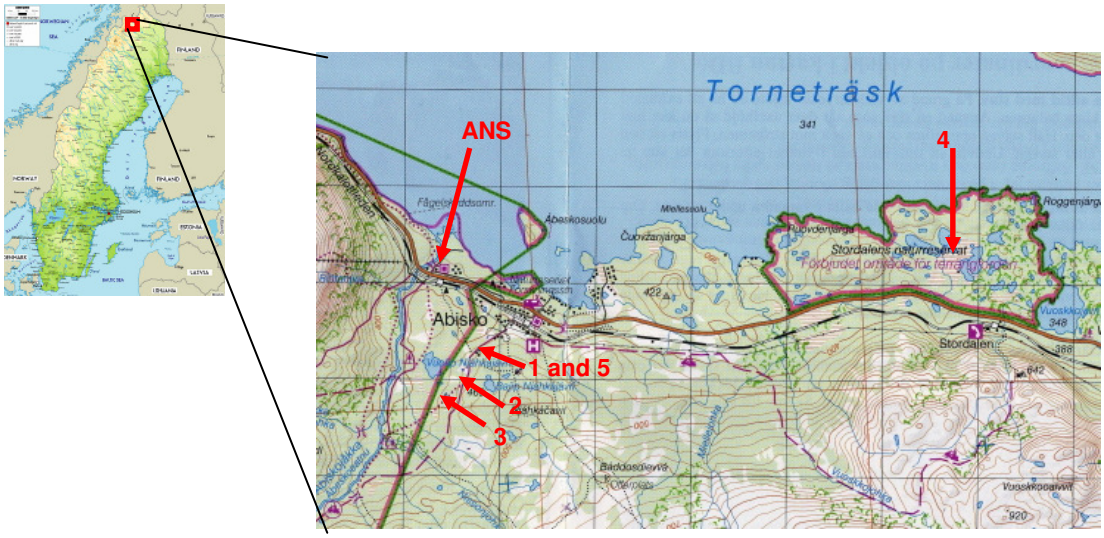


Figure 5.1: Map to show the general sampling area at Abisko, Sweden and the location of the individual sampling sites (numbered) used in the 2007 and 2008 measuring campaigns.

In the initial set of measurements, in August 2007, air samples were collected from 15 sampling points situated within 5 different wetland locations, Figure 5.1. Four locations were 1.5 km south of ANS, at elevations between 420 and 440 m a.s.l. (average precipitation 304 mm p.a), whilst the fifth location was Stordalen Mire, 10 km east of ANS, at 360 m a.s.l. (average precipitation 400 mm p.a.). The sun was above the horizon between 18.5 and 20 hours per day during the two week sampling period and there was no complete darkness. The individual sampling points within a location were chosen to capture the differences in hydrology and vegetation at that location. Broadly these could be divided into wet areas, dry areas and damp areas. A summary of the major types of vegetation present in each category is given in Table 5.1. An example of the vegetation at the dry, damp and wet sampling points in the mid-growing season and just before vegetation growth at the start of the growing season in shown in Figure 5.2.

Table 5.1: Classification of sampling sites according to hydrological condition and main types of vegetation present at the sampling sites.

Water conditions	Main plant species present
Wet	*Carex rostrata*, bryophytes
Damp	*Equisetum palustre,* sphagnum mosses
Dry	*Vaccinium spp., Betula nana, Empetrum nigrum, Andromeda polifolia, Eriophorum spp*., *Rubus chamaemorus,* lichens, bryophytes

Figure 5.2: Example sampling points; dry areas in mid-growing season (a) and pre-growing season (b); damp areas in mid-growing season (c) and pre-growing season (d); wet areas in mid-growing season (e) and pre-growing season (f).

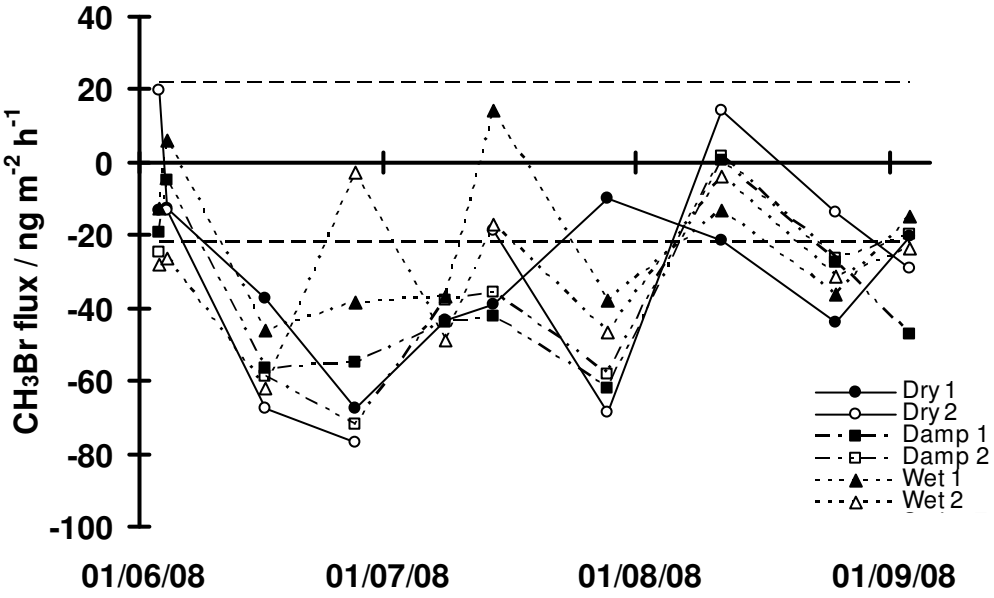
5.2 Sampling methods

Regular two-weekly measurements were made throughout the full 2008 sub-Arctic growing season (June–September 2008) at two of the locations 1.5 km south of ANS used in the initial study. There were six sampling points in total, two each in areas designated as wet, damp and dry. The hours of daylight varied over the study period. Until 23/07/08 the sun never set, thereafter declining to 15 h per day above the horizon by 04/09/08. However, even under clear-sky conditions sampling sites were not necessarily exposed to direct sunlight because of shadowing from surrounding mountains. The air samples were analysed by GC-ECD as described in Chapter 2.

5.3 Seasonal trends in methyl halide flux from Abisko, Sweden

Figure 5.3 shows the time series of net CH_3Br and CH_3Cl fluxes during the 2008 growing season for those measurements made within the time period 10:00–16:30 on each occasion. These data constitute the first full-season time series of methyl halide fluxes at high latitude. Seasonal variation is apparent for both CH_3Br and CH_3Cl, with flux magnitudes changing most markedly through June and early July, corresponding to the most active period of the growing season, and smallest net fluxes at the beginning and end of the growing season.

(a)



(b)

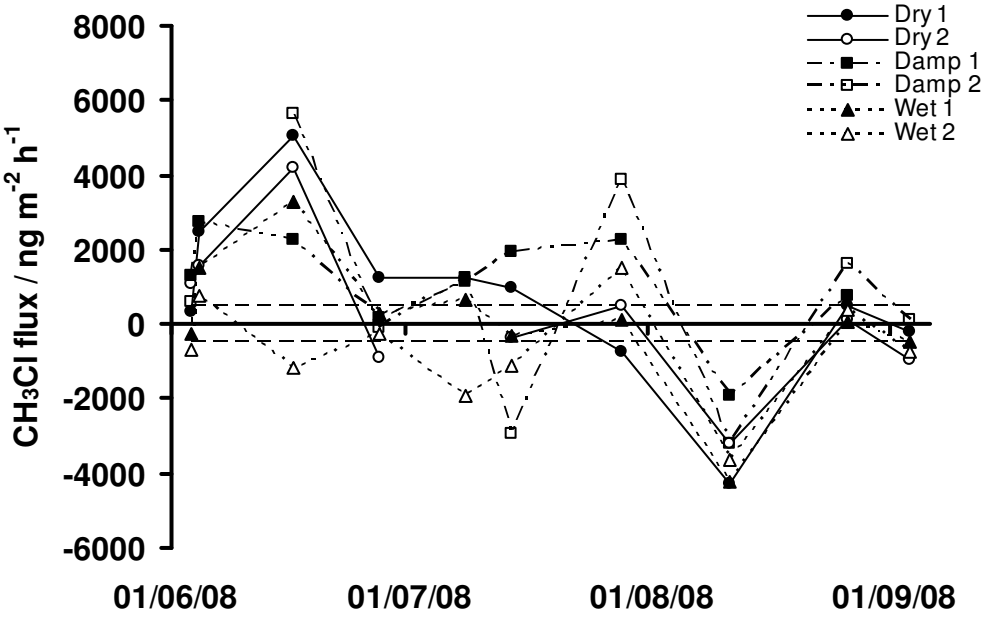


Figure 5.3: Time series of (a) net CH_3Br flux and (b) net CH_3Cl flux from six sampling points during the 2008 growing season. Horizontal dashed lines indicate limits of detection for CH_3Br and CH_3Cl net flux determination.

5.4 Daily trends in methyl halide emissions from Abisko, Sweden

Figure 5.4 shows the net CH_3Br and CH_3Cl fluxes measured at four-hourly intervals over a 24 h period on 04/06/08 from collars 'Wet 2', 'Dry 2 and 'Damp 1'.

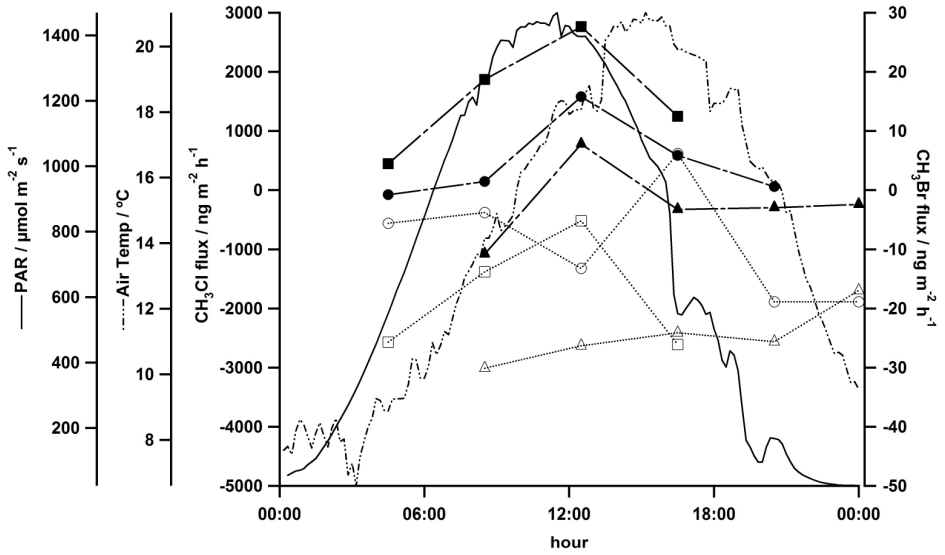


Figure 5.4: CH_3Br (open symbols) and CH_3Cl (solid symbols) fluxes from sites 'Wet 2' (circles), 'Dry 1' (squares) and 'Damp 1' (triangles), together with ambient air temperature and PAR, measured over a 24 hour period on 04/06/08. Limits of detection for net flux determination are ±21 ng m^{-2} h^{-1} and ±490 ng m^{-2} h^{-1} for CH_3Br and CH_3Cl, respectively.

CH_3Br fluxes were very small during this sampling period and there was no significant diurnal flux trend for any of the three sites. In contrast, there was some diurnal variation in CH_3Cl fluxes, with a peak occurring around the middle of the day for all three sites investigated. Air temperature varied from a low of 8.9°C (averaged across sites) at 00:30 to a high of 20.5°C at 16:30 and soil temperatures followed a similar cycle. The lag between peak temperature and peak CH_3Cl emissions is consistent with the paradigm of uptake and emission processes occurring simultaneously (Section 5.3). Peak emissions related to plant activity occur when there is most light, around midday, but as soil temperatures increase, soil-based bacterially-mediated uptake processes increase, reducing the net flux to the atmosphere.

Aside from the diurnal cycle in net CH_3Cl flux noted above, no substantial correlations between CH_3Br or CH_3Cl flux and air temperature, enclosure

temperature, sub-surface temperature or PAR were discernible for the time series data in this study. It is inherently difficult to tease out any such relationship(s), if they exist, from *in situ* field data due to uncontrolled confounding between these factors (e.g. temperature and PAR) and with other factors (e.g. date during season and individual site characteristics). However, the magnitude of CH_3Cl fluxes did differ significantly (ANOVA) between locations classified according to their hydrology and vegetation (Figure 5.4). Mean (±1 sd) CH_3Cl fluxes from each of the pairs of locations designated 'Wet', 'Damp' and 'Dry' were -160 ng m^{-2} h^{-1}, 1300 ng m^{-2} h^{-1} and 620 ng m^{-2} h^{-1}, respectively. These averaged values mask an important observation from Figure 1 (b) that locations classified as 'Dry' had the greatest seasonal range in fluxes, having generally greater net emission of CH_3Cl than other sampling points in the early part of the season, but greater net uptake of CH_3Cl in the latter part of the season. CH_3Br fluxes did not differ significantly with hydrology/vegetation classification, although there was a non-significant tendency for greater CH_3Br uptake at drier sites, Figure 5.2 (a).

5.5 Summary

A seasonal variation in net CH_3Br or CH_3Cl fluxes, as observed here, was not reported by Rhew *et al.* (2007) for their coastal Alaskan Arctic tundra site, but their measurements only spanned the period late-June to August. The sampling sites at Abisko were generally a net sink for CH_3Br. The mean (±1 sd) net CH_3Br flux for the data shown in Figure 1 is -30 (±25) ng m^{-2} h^{-1} (n = 60), with greatest net uptake coincident with the longest days in late June and early July. Including all flux measurements made during daylight hours between June and September at these sites yields an overall mean (±1 sd) net CH_3Br flux of -25 (±20) ng m^{-2} h^{-1} (n = 92). The similar mean fluxes for the full and subset of measurements is consistent with the interpretation that any diurnal variability is insignificant compared with variability on the week-to-week time scale and between sites. The small net uptake of CH_3Br observed at these high-latitude wetlands contrasts with the net emissions measured at wetland and peatland areas in Scotland (Hardacre, unpublished data), Ireland (*Dimmer et al.*, 2001) and New Hampshire, USA (*Varner et al.*, 1999) but is consistent with the net CH_3Br uptake reported for Arctic Alaskan tundra (*Rhew et al.*, 2007; *Teh et al.*, 2009). These two latter studies reported an average net CH_3Br flux of

-18 ± 22 (n = 40) and -45 ± 60 (n = 36) ng m^{-2} h^{-1} (converting these authors' standard errors to standard deviations for comparison with presentation here).

During the initial study at Abisko in August 2007, the mean (±1 sd) net CH_3Br flux was -17 (±17) ng m^{-2} h^{-1} (n = 16, data not shown). Comparing this with the average flux in August 2008 of -13 (±19) ng m^{-2} h^{-1} (n = 16) shows there was no substantive inter-annual variation in CH_3Br flux between these two years. In the Alaskan studies, the greater net uptakes of CH_3Br and CH_3Cl observed in 2006 than in 2005 was attributed to the higher soil temperatures in 2006 (*Rhew et al.*, 2007; *Teh et al.*, 2009).

The seasonal pattern of CH_3Cl net fluxes at the Abisko sites was different to that of CH_3Br (Figure 5.2). Net emission of CH_3Cl was generally observed during the period early-June to late-July (except at collar 'Dry 2'), with more net uptake later in the season. Measurements on 11/08/08 showed comparatively large uptake of CH_3Cl at all sites. There was no obvious reason to doubt the authenticity of these data. On average, net flux was positive: mean (±1 sd) net CH_3Cl flux for the data shown in Figure 1 was 550 (±1800) ng m^{-2} h^{-1} (n = 60), or 400 (±1600) ng m^{-2} h^{-1} if all 92 measurements made during daylight hours are included. Again the comparable mean values demonstrate that seasonal and spatial differences dominate the flux variability. Likewise, the larger relative standard deviation in the CH_3Cl flux measurements compared with the CH_3Br flux measurements reflects the larger seasonal variation in the former than in the latter. The small net emission observed for CH_3Cl on average across 6 sampling points and the whole growing season at Abisko is consistent with observations of emissions, on average, in Scottish wetlands (Hardacre, unpublished data) and Irish peatlands (*Dimmer et al.*, 2001) but in contrast to average net CH_3Cl uptakes of 637 (±610) ng m^{-2} h^{-1} (*Rhew et al.*, 2007) and 1240 (±1350) ng m^{-2} h^{-1} (*Teh et al.*, 2009) reported for the Alaskan tundra sites (again converting these authors' expressions of variability into standard deviations).

An association between hydrology and methyl halide fluxes has been reported previously. Both Rhew *et al.* (2007) and Teh *et al.* (2009) measured greater CH_3Br and CH_3Cl uptake at drier locations in their studies in Alaskan tundra, with the latter reporting that water table depth was the best predictor of both net and gross CH_3Br and CH_3Cl uptake. On the other hand, Redeker and Cicerone (2004) reported that low

water conditions in rice paddies, another highly moist environment, enhanced net CH_3Br and CH_3Cl emission from certain rice cultivars. The current field study does not distinguish whether the difference in CH_3Cl (and CH_3Br) fluxes between sites was driven by the vegetation or the hydrological status, but it is likely that both are relevant as there was not a consistent trend in CH_3Cl flux from wet to dry soil conditions.

The picture that emerges from consideration of this study in Swedish high-latitude wetlands, and the studies in Arctic Alaska (*Rhew et al.*, 2007; *Teh et al.*, 2009) and New Hampshire peatlands (*White et al.*, 2005) (together with further data from wetlands and peatlands in Scotland) is of land-atmosphere CH_3Br and CH_3Cl fluxes in such systems being the net result of plant- and soil-mediated emission and soil-mediated uptake; and that the relative magnitudes of each varies with the micro-topology of the site (i.e. with vegetation and hydrology) and with time during the season. The latter factor impacts on vegetation activity and hydrology. Soils at the start of the season at Abisko are wetter than subsequently due to snow and ground-ice melt, so soil uptake rates are lower, yet plant-related activity is higher. The net flux is dynamically sensitive to changes in soil moisture and biological activity as the season progresses through to drier but cooler conditions and decreased vegetation growth. This picture is consistent with the observation by Teh *et al.* (2009) that the limitation on methyl halide uptake in saturated soils is due to mass transfer limitation rather than reduced microbial activity under anaerobic conditions. It is also consistent with the suggestion that measurements of CH_3Cl fluxes which miss the beginning of the growing season in these ecosystems will likely show averaged net negative flux overall.

When comparing the results from this study site with those in Alaska (*Rhew et al.*, 2007; *Teh et al.*, 2009), it is also important to remember that the Abisko sites, although within the Arctic Circle, differ from the Alaskan sites not only biogeographically but in being classified as sub-Arctic in terms of vegetation cover and climate rather than Arctic. The warmer sub-Arctic climate, and generally greater vegetation cover, appears to result in small net CH_3Cl emissions prevailing at Abisko when integrated over the full growing season and all sites, consistent with

observations of net CH_3Cl emissions overall in other comparatively high-latitude wetlands in Ireland (*Dimmer et al.*, 2001) and Scotland (Hardacre, unpublished).

5.6 Global Implications

Rhew *et al.* (2007) estimated net annual uptake rates of 0.3 Gg CH_3Br and 11.2 Gg CH_3Cl for tundra worldwide assuming a total tundra surface area of 7.3×10^{12} m^2 and that their average net fluxes of -18 ng CH_3Br m^{-2} h^{-1} and -637 ng CH_3Cl m^{-2} h^{-1} applied over a 100-day growing season to all such ecosystems globally. The CH_3Br flux data from this study suggest that this CH_3Br estimate does not need to be revised. However, the small net CH_3Cl emission observed in this work suggests that the previous extrapolated global net uptake estimate for CH_3Cl may need to be revised downward to take account of these data for the Swedish sub-Arctic.